SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

TREATMENT OF IRON IN GROUNDWATER USING PEBBLE SIZE AND SAND SIZE MARBLE COLUMN FILTER

By

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DECLARATION

I hereby declare that I conducted, completed the research work and written the dissertation entitled “Treatment of Iron in Groundwater Using Pebble Size and Sand Size Marble Column Filter”. I also declare that is has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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Date :

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PERAWATAN FERUM DALAM AIR BAWAH TANAH DENGAN FILTER LAJUR BATU MAMAR BERSAIZ PEBBLE DAN PASIR

ABSTRAK

Air bawah tanah merupakan sumber air sekunder di Malaysia. Isu kekurangan air telah menjadi isu besar semasa musim kekeringan dan ia telah menjejaskan kesejahteraan hidup seharian kita. Air bawah tanah adalah sumber air yang berpotensi untuk mengatasi isu kekurangan air sebab selama ini sumber air yang digunakan adalah air permukaan tanah sahaja. Di negeri Pulau Pinang, isu kekurangan air jarang berlaku tetapi sumber air yang baru perlu dieksploitasikan supaya dapat mengatasi penambahan kegunaan air pada masa kelak. Di Kampus Kejuruteraan USM, Nibong Tebal, air bawah tanah berpotensi untuk dijadikan sumber tali air. Kajian ini akan mengkaji tentang pra-rawatan air bawah tanah untuk meresapkan ferum dalam air dengan menggunakan filter batu mamar lajur yang bersaiz “pebble” dan pasir yang merujuk kepada klasifikasi saiz partikel Wenworth. Air bawah tanah dirawatkan dengan filter batu mamar lajur untuk memastikan peresapan ferum dalam air bawah tanah. Kadar aliran optimum dipastikan dari keputusan peresapan elemen pencemaran dalam air yang telah dirawat. Dalam kajian tersebut, air bawah tanah disalurkan dari perigi yang berlokasi dalam Kampus Kejuruteraan USM, Nibong Tebal. Batu mamar yang digunakan adalah batu mamar bermutu tinggi yang mencapai gred ketulenan $CaCO_3$ 97.3%. Sebelum eksperimen dimulakan, pencirian air bawah tanah telah dijalankan dengan menggunakan Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analisis manakala batu mamar telah dicirikan dengan X-Ray Fluorescent (XRF) analysis dan Scanning Electron Microscopy (SEM). Empat kadar aliran iaitu 0.017, 0.011, 0.008 and 0.007 L s^{-1} telah dikaji. ICP-OES mencirikan ferum dan elemen lain dalam sampel air asal dan sampel air lepas rawatan. Dari kajian tersebut, didapati kadar aliran 0.007 L s^{-1} adalah kadar aliran optimum untuk meresap ferum dalam

air bawah tanah. Partikel bersaiz “pebble” didapati tidak berkesan seperti partikel bersaiz pasir untuk merawatkan air bawah tanah tersebut. Kadar aliran yang meresapkan terbanyak ferum adalah kadar aliran 0.007 L s-1. Penumpuan ferum dalam air telah menurun ke 0.013 ppm dari 1.999 ppm. Batu mamar adalah media peresapan yang berpotensi untuk dijadikan media peresapan pra-rawatan air dengan harga murah dan peresapan yang efektif.

TREATMENT OF IRON IN GROUNDWATER USING PEBBLE SIZE AND SAND SIZE MARBLE COLUMN FILTER

ABSTRACT

Groundwater has always been a secondary water source in Malaysia. Water shortage during dry seasons had become a big issue that affecting the daily activities of the public. Groundwater is potentially a secondary water source that could ease the situation of water shortage since the current water supply comes from surface water. In Penang state, the water shortage issue does not happen frequently yet the new water resource should be explored to meet the demand of public water supply in future. In USM Engineering Campus, Nibong Tebal, there is groundwater resource beneath which has the potential to be developed for irrigation water use. This project studies about the pre-treatment of groundwater, which is removal of iron from the groundwater using pebble size and sand size marble column filter as referring to Wenworth particle size classification. The groundwater is treated using marble column filters to determine the removal of iron and other contaminant from the groundwater. Optimum flow rate is determined from the results of contaminants removal percentage when using different flow rate. In this project, the groundwater is sampled from the monitoring well located in USM Engineering Campus, Nibong Tebal. The marble used as filter media is high grade marble with 97.3% of $CaCO_3$. Before the experiment is start, the groundwater is characterized using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis whereas the marble is characterized by X-Ray Fluorescent (XRF) analysis and Scanning Electron Microscopy (SEM). The filtration is then run with 4 different flow rates which are 0.017, 0.011, 0.008 and 0.007 L s^{-1}. ICP-OES analysis determines the initial and final concentration of iron and other element in the water sample. The results had reported 0.007 L s^{-1} as the most effective flow rate for iron removal in the

groundwater. As seen from the results, pebble size marble is less effective in contaminant removal compare to sand size marble. The highest removal percentage of iron is for the sand size marble column filter when the flow rate is 0.007 Ls^{-1}. The initial concentration of iron in the groundwater is 1.999 ppm but end up with 0.013 ppm of iron left in the water after filtrated. The marble is possible to be a cheap and effective filter media for iron removal in development of groundwater pre-treatment process in USM as the results show high removal for iron so as other element in the groundwater.

CHAPTER 1

INTRODUCTION

1.1 Background

Groundwater is a supplementary source of freshwater in Malaysia which is cleaner than surface water, although it only consists of less than 10% of the public water supply source in the nation (Abd-Razak Y, 2009). Being as the alternative source of water, the importance of groundwater is getting more significant as the available source of surface water is insufficient to supply the demand of public water usage. Prolonged dry seasons, unmatched water supply, growing population with increasing demand of water and lack of river basin management had become factors that causes water crisis in Malaysia (Abdul Rahman, 2014). Instead of depending on single source of surface water, the alternative source which is groundwater could help to solve the crisis of water shortage yet the research and investigation on groundwater source need to be strengthened.

The groundwater is pumped from an aquifer under the ground and it is generally less contaminated compare to surface water yet contaminants such as heavy metals, nitrates, volatile organic compounds and pathogens had threatened the quality of groundwater. Iron is the heavy metal chosen to be treated as in the collected sample groundwater because it is a dominant heavy metal that had exceed threshold limit for potable water standards set by United States Environmental Protection Agency (EPA). This project will study about removal of iron by adsorption on marble and the efficient particle size of limestone for iron removal.

Groundwater is an important source of freshwater which requires less treatment than surface water. Although groundwater is less contaminated, it is still susceptible to contaminants and it requires suitable water treatment to remove contaminants such as heavy metals, aromatic hydrocarbons, metals, volatile organic carbons, nitrates, microorganisms etc. in the water. Many technologies are established to treat groundwater and the cost for water treatment is biggest concern for the design and implementation of a groundwater treatment system.

In conventional water treatment plant, a high capital cost is spent on reverse osmosis (RO) filtration system treatment to decrease dissolved minerals besides removing taste, colour and odour-producing organic compounds in the water. The water treated by RO filtration system is suitable for household use as RO membrane can remove virtually all microorganism in water. Besides RO filtration system, AC could be a potential material used in water treatment system to remove contaminants just like the RO membranes yet the capital cost is estimated to be much lowered. The available technologies for public water treatment is mainly depending on RO filtration system currently, yet the pre-treatment process for the raw water is always manipulated by the suitability of treatment method and media to remove the contaminant to certain extent economically.

Heavy metal contamination in water source has many negative impacts on human health. Heavy metal is a term assigned to metals and metalloids that having high atomic density five times greater than water molecules, or at density higher than 4000 kg m^3 (Hashim et al. 2011). Heavy metals such as iron, manganese, lead, cadmium, arsenic and mercury are commonly found in groundwater. These heavy metals came from natural dissolution of minerals and human activities. Although heavy metals such as iron, manganese, selenium and chromium are essential micronutrients in human body, the daily intake of these elements are recommended under certain limits in concern of keeping a healthy life.

Iron is a key micronutrient for a good metabolism as it is an essential component to build proteins and enzymes in human body. U.S. Food and Nutrition Board have established a guideline on upper limit of 45 mg iron intake per day is a safe limit to most group of people but somehow the iron in water below 3 ppm will not bring health risk to the consumers as claimed by U.S. Food and Nutrition Board.

Iron is one of the most common element on Earth crust and accounts for over 5 percent of the Earth's crust by weight. When an aquifer contacts with rock rich in iron minerals, the solids dissolve and will release iron into the groundwater. At concentration of 0.3 ppm is the threshold limit of iron in treated water following international standard of US EPA. Iron exists in dissolved state or ferrous ion under low oxygen level, particularly in deep aquifers or at low pH. The ions exist as ferric state when oxygen level is greater than 1-2 ppm or when the pH condition is acidic. Most of the treatment plant applied oxidation treatment method on soluble iron by adding oxidizing agent like potassium permanganate (IV) $KMnO_4$ into raw water and iron will precipitate for physical filtration.

Physical adsorption is a common method adapted to remove metal contaminants in raw water. The common media for physical adsorption includes activated carbon, sand, rice hulls and some other rock adsorbents such as limestone. In this study, marble taken from Zantat Sdn. Bhd. in Simpang Pulai, Perak will be used as adsorption media in the column water filter. The groundwater is pumped out from aquifer and allowed it to contact with open air for oxidation of iron (II) under aerobic condition where in this sample ferrous sulphide FeS is formed. The FeS solid will be treated by using a column filter which applying physical adsorption of metals on marbles.

Limestone, which carries similar chemical properties as marble is widely used as material for water treatment throughout the world. It is used in acid mine drainage (AMD) treatment to increase pH of AMD, also used to neutralize acidity in industrial wastewater. There are few physicochemical factors which control the effectiveness of water treatment using limestone such as co-precipitation of metal ions or adsorption, redox processes, pH fluctuation and dilution of groundwater by mixing with limestone (Mandadi, 2012). In this study, the major factor controlling the efficient of iron removal is the adsorption of iron on marble. Different sizes of marble are used as filter media in a column filter which could determine the efficient of iron removal using different sizes marble chips.

1.2 Objectives

This research project is a study on removal of soluble iron from groundwater using marble as adsorbent by physical adsorption. High purity marble and limestone which mainly composed of calcite $CaCO_3$ (67-90% CaO) has a potential to be a cheap and effective material to treat heavy metals in water as shown from previous studies (Yao Zhigang, 2009).

The major objectives of this study were as follows:

I. To treat iron in groundwater using pebble and sand size marble column filter.

II. To investigate the optimum flow rate to remove iron from groundwater using marble pebble and sand column filter.

1.3 Scope of Work

Groundwater sample were pumped out from groundwater well located in USM Engineering Campus for groundwater composition analysis using ICP-OES. The contamination level was determined from results of ICP-OES analysis and method of treatment is studied.

Marble sample are taken from Zantat Sdn. Bhd. located at Simpang Pulai, Perak. The marble sample are characterized for its composition using XRF. The physical characterization for crystal structure, agglomeration and size of ground marble is done by SEM. Different sizes of marble pebbles and sand are obtained by crushing and sieving marble rocks.

The experiment started by running groundwater in the column filter with marble in pebbles and sand sizes as adsorbent. The treated water is tested for elements composition using ICP-OES again to observe efficiency of iron removal from groundwater.

1.4 Thesis Outline

This thesis is organized into five chapters. Chapter 1 gives brief introduction that focuses on the background of groundwater treatment with marble as filter media, and emphasis on the objectives, scope and problem statements of this study. Chapter 2 further elaborate the groundwater resource in USM Engineering Campus, marble column filter, and the heavy metal contaminants in the groundwater. Chapter 3 includes the details research methodology such as sample preparation, laboratory work, groundwater characterization and backwash of column filter. In Chapter 4, results of filtration and water quality parameters are presented. Finally, Chapter 5 consists of recommendation and conclusion for future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Groundwater

2.1.1 Resources

Groundwater in Malaysia is the secondary source of freshwater since decades ago which covered less than 10% of public water supply in the nation (Abd-Razak Y, 2009) and the demand of groundwater supply might rise as major source of freshwater in certain states which included Kelantan, Pahang, Terengganu, Sabah and Sarawak (Nampak, Pradhan and Manap, 2014). Certain island in Malaysia such as Kapas and Manukan Island has only groundwater as their water source. The reliance on groundwater varies among different countries, and it is estimated as freshwater supply to one third of the world population for their daily activities (Hiscock, 2011).

Malaysia has not strongly depending on groundwater as source of public water supply yet there are rich resources of groundwater in Malaysia with high recharge rate from over 2800 mm of rainfall annually. More attention is needed to concern about contamination like heavy metals and pathogens in groundwater and its treatment method to remove the pollutants before it risks the health of consumers.

Therefore, it is necessary to have more study on groundwater to manage the groundwater supply and aquifers around Malaysia. The study on groundwater treatment methods will have an impact in improvisation or lowering cost of groundwater treatment system in Malaysia to transform groundwater into a reliable and sustainable public freshwater supply.

2.1.2 Contamination

Most aquifers are contaminated because of development and industrial activities of human. The pollutants found in groundwater can be natural or human-induced chemicals like pesticides, herbicides, fertilizers, landfill leachates, human or animal sewage, leakage from septic tanks, chemical and road salts which seeped into shallow aquifers during groundwater recharge process. The groundwater with high level of contaminants are not suitable for uses. As for drinking, total dissolved solids (TDS) concentration as a measure of the combined content of all inorganic and organic substances in the water should not exceed 1000 mg/l as suggested by American Health Association. The sources of dissolved solids in water are minerals constituents from soils and rocks, the water with TDS concentration above 1000 mg/l is not acceptable for most uses.

The contaminants in water could be classified as inorganic, organic and microbiological contaminants. The inorganic contaminants are metals, nitrates like aluminium, arsenic, chloride, cyanide, mercury, dissolved solids, iron, lead etc. which could come from industrial waste or naturally occurred with the geological environment of the aquifer. The organic contaminants are volatile organic compounds, pesticides, phenols, plasticizers, chlorinated solvents, benzo[a]pyrene and dioxin. Microbiological contaminants in groundwater are coliform bacteria which occur naturally in the environment from soils and plants and in the intestines of humans and other mammals. These contaminants will bring impact on the consumers' health and hence they must be removed from the public water supply. Certain contaminants such as iron and manganese will cause the water to have a pungent odour and causing the water to have unfavourable precipitates which will leave stains at plumbing fixtures, fabric or equipment.

EPA has categorized the drinking water contaminants into four general categories as listed in Table 2-1 together with examples of the contaminants. Some of the contaminants poses health risk to the consumers while some of the contaminants are harmless to consumer. A list of Contaminant Candidate List (CCL) is establish by EPA to serve as first level of evaluation for unregulated water contaminants that require investigation and research of potential health effect.

Table 2-1: Types of Drinking Water Contaminants and Examples

Type of Contaminant	Examples of Contaminant
Physical	Sediment, organic material suspended in water which came from erosion.
Chemical	Elements or compounds i.e. nitrogen, bleach, salts, pesticides. Metals, toxins from bacteria, and human or animal drugs.
Biological	Microbes i.e. bacteria, viruses, protozoan, and parasites.
Radiological	Elements which can emit ionizing radiation i.e. caesium, plutonium and uranium.

2.1.3 Heavy Metal Contamination

Heavy metals in groundwater came from dissolution of minerals in soil, landfill leachate, sewage, industrial spills and leaks, deep-well disposal of liquid wastes, and leachate from mine tailings. The soil provides an environment which will influence the contamination of aquifer with a variety of reactions. There are many factors which will affect the rate and extent of the contamination, these factors including pH, Eh, temperature, moisture, complexation with other soluble constituents, ion exchange capacity and organic matter content.

The removal of iron from groundwater is the main point to be focused in this study. Iron is categorized as heavy metal contamination just like manganese, lead, cadmium, arsenic and mercury. Based on the drinking water standards establish by EPA, the content of iron should not exceed 0.3 ppm so as the water quality standard for industrial uses. At 0.3 ppm, the health risk of dissolved iron in drinking water is insignificant. Certain agency had established standards of water quality for industrial uses, i.e. China Environmental Agency had established Industrial-Use Water Standard (GBT19923-2005) on 2006, the limit of iron for industrial-use water is limited to below 0.3 ppm just alike to drinking water standards.

Iron (II) in deep aquifer will oxidize to iron (III) to form rust-coloured precipitates which will be removed by physical or gravity water treatment. The oxidation occurs naturally at alkaline pH and when the dissolved oxygen level is greater than 1-2 ppm. Unlike iron (II), iron (III) is not soluble in water. Chlorine is commonly used as an oxidizer for iron (II) to become iron (III) because it also provides protection from microbial contaminants.

2.1.4 Indication of Good Quality Groundwater

Quality of water is important to know whether the water is suitable for what uses, only the water which fulfilled drinking standard criteria can be used as drinking water. The quality of water can be determined by measuring biochemical demand oxygen (BOD) of water, total dissolved solid (TDS), turbidity, salinity, ammonia concentration, pH, coliform test, organic contaminants measurements and inorganic contaminants measurements. The method of treatment is different when the contaminant in the water source is different. Usually physical method is applied to remove solids in water, followed by chemical method to remove soluble ion and molecules. The viruses or bacteria are removed by chlorination or ultraviolet treatment, some coliform can also be removed by physical adsorption method.

2.1.5 Groundwater in USM Engineering Campus

Groundwater in USM Engineering campus is stored in alluvial aquifer under the ground. This groundwater has not been a source of water as the groundwater need to be treated before it can be used as non-potable or potable water. USM Engineering Campus is located at Nibong Tebal, Pulau Pinang which has geologic feature of weathered granite, mainly alluvial soil on the surface layer of ground. The recharge of groundwater could possibly come from surrounding rivers like Sungai Kerian which extent to the sea or the few retention ponds in USM Engineering Campus besides the natural recharge of surface water from rain.

The surrounding of USM Engineering Campus had been palm oil plantation for years. A chicken farm had also established at northern part in distance within 1 km from the campus. Therefore, the groundwater in USM Engineering Campus are susceptible to be contaminated by phosphates and nitrates in fertilizer and pesticides used to control palm oil plantation or livestock feeding. The contamination concentration and recharge rate of aquifer will have changes between dry season and rainy season as groundwater recharge is strongly depending on climate and topography of the area (Sophocleous, 2002). The groundwater is potentially to become a non-potable water source for daily uses in USM Engineering Campus upon development of proper water treatment process.

2.2 Groundwater Treatment

2.2.1 Treatment Method and Technology

Groundwater treatment, also called as groundwater remediation can be categorized into three classes: i. Chemical Treatment Technologies, ii. Biological Treatment Technologies, iii. Physicochemical Treatment Technologies (Hashim *et al.*, 2011). Most groundwater treatment system utilize a combination of technologies. The most widely used groundwater remediation is Pump and Treat, a physical treatment where the groundwater is pumped to the surface and couple with either biological or chemical treatment to remove contaminants. Table 2-2 listed some of the common technologies used in groundwater treatment as reviewed (Hashim *et al.*, 2011).

Table 2-2: Water Treatment Categories and Technologies

Chemical	1. Reduction 2. Chemical flushing 3. In-situ chemical fixation
Biological	1. Biological activity in the subsurface 2. Enhanced biorestoration 3. Biosorption
Physicochemical	1. Permeable reactive barriers (sorption in, precipitation, biological barrier) 2. Adsorption, absorption, filtration 3. Electrokinetic treatments 4. Others

Different kind of technologies or method will have different effectiveness on removal of different heavy metal in the groundwater. Therefore, a groundwater treatment plant is designed to treat particular groundwater with selected technologies and methods. The cost and technologies in treatment are strong factors which caused the restriction on groundwater application for daily usage in poor countries.

2.2.2 Physicochemical Adsorption

Physicochemical adsorption is a common method adapted to remove metal contaminants in raw water. It is cheap and easy treatment method. The common media for adsorption are activated carbon, sand, rice hulls, zeolite and some other rock adsorbents such as limestone. Physicochemical adsorption is physical remediation to remove contaminants in groundwater where the media or adsorbent provides a site to adsorb constituents in groundwater. Previous studies had proved activated carbon is an adsorbent with large capacity which effectively remove microbes and inorganic pollutants in water (Bhatnagar *et al.*, 2013) yet an effective adsorbent for heavy metals removal is still under studies.

In this study, marble at different size range will be used as adsorbent or media to remove iron from groundwater. The soluble iron undergone aerobic oxidation after pumped out from aquifer, it precipitates to form blackish ferrous sulphide with pungent smell or oxidized to form precipitate of iron hydroxide. The efficiency for marble at different sizes in removing iron from groundwater will be studied.

At years before 1970s, a physicochemical treatment process usually involves steps as listed in Figure 2-1 (Manahan, 2000).

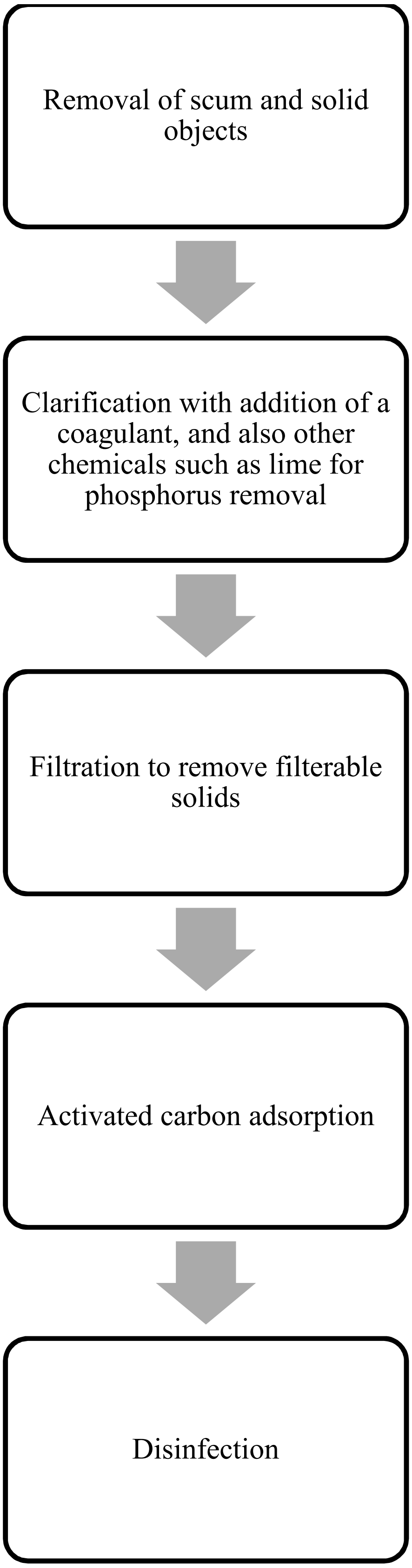

Figure 2-1: Steps of Physicochemical Treatment

However, the development of biological treatment after 1970s had contrasted physicochemical treatment appeared to have higher chemical and energy cost for energy consumption of treatment plant, raw materials cost and backwash cost (Manahan, 2000). The development of technologies in physicochemical treatment technologies is getting important lately as it should apparently a cheaper treatment process comparatively as it has possibilities to use cheap raw materials which can easily obtained at every place as adsorbent. A low-cost groundwater treatment process is important to provide cheap clean water supply at rural areas which is a long-term crisis happening all the time.

2.2.3 Parameters for Effective Adsorption

The effectiveness of iron adsorption on the marble particle surfaces is strongly depending on few parameters such as contact time on adsorption, pH/Eh of water, temperature, adsorbent material, adsorbent size and initial concentration of contaminant.

A study of mine water treatment using limestone has conducted a continuous removal of manganese using powdered limestone. The iron in the mine water reduced from 2.20 ppm to 0.73 ppm for resident time of 60 minutes in condition with blending of 125 ppm of limestone and 67 ppm of carbonate ions with initial pH of 6.5 and final pH increased to 8.6. The pH control and carbonate concentration is key parameter for precipitation of metals in the mine water (Silva *et al.*, 2012).

2.3 Marble

2.3.1 Mineralogy

Marble is a type of metamorphic rock which is altered from limestone under heat and pressure. It is mainly composed of a carbonate mineral, which is calcite ($CaCO_3$), dolomite and aragonite. The impurities in limestone such as sand, clay, iron oxides and sometimes organic matters will affect the colour of marble after metamorphism. It is common to have white, pink and black marble. The hardness of marble on Mohs Hardness Scale vary from 3-4. High-grade marble is used to make valuable products like marble tiles, marble wall and sculptures. Lower grade marble which has cracks or has lower metamorphism is normal to be categorized as limestone for the applications as they do not carry values as high-grade marbles.

2.3.2 Uses of Calcite and Limestone in Water Treatment

Marble chips are studied for its uses in water treatment since it has alkali properties to act as pH regulator in acidic water just as limestone. Besides hardness, marble has similar chemical properties like limestone. It is common to find limestone used by industry in water treatment process such as acid mine drainage treatment and neutralizing industrial wastewater. Different kind of limestones such as pure limestones, brecciated limestones and carbonaceous limestone carry different degree of effectiveness in heavy metal removal (Yao Zhigang, 2009). Limestone is also applied in an AMD treatment located at Gangneung, Korea since 1999 and it successfully maintain effective long-term treatment where physicochemical process of co-precipitation/adsorption with iron hydroxide in the AMD stream is a main control variable of the process (Shim *et al.*, 2015). Hence, limestone has a strong potential in treating heavy metals from water. The selection of limestone type in a treatment is depending on the purpose of the water treatment.

2.3.3 Adsorption of Metal

In a previous study, pure limestone (CaO 67% - 90%) with sodium carbonate injection had shown a great ability to remove cadmium, copper, nickel and zinc from mine water at efficiencies of 58.6% for Cd, 100% for Cu, 47.8% for Ni, and 36.8% for Zn at 20^{o}C, with optimum pH about 8.9 to 9.1 (Yao Zhigang, 2009). The co-precipitation of heavy metals had ease the adsorption process. The application of raw limestone in AMD treatment also shows that limestone could increase and stabilized the pH of AMD, with precipitation of iron hydroxide from the AMD stream (Shim *et al.*, 2015). The precipitated iron in groundwater is potentially to be removed using limestone as an adsorbent in this physicochemical method. Different types of limestone and different sizes of limestone will have different adsorption efficiency of iron. The difference of heavy metal removal efficiency between grain size of 0.55 – 0.25 mm and 0.25 – 0.18 mm show a small difference only which is considered as that there is no obvious change in removal efficiency with decreasing size of limestone (Yao Zhigang, 2009).

2.3.4 Marble in Simpang Pulai, Perak

Simpang Pulai is located at central part of Perak, Malaysia and has a distance of 13 km away from Ipoh town as shown in Figure 2-2. The Ipoh city located in Kinta Valley which is has bedding and surrounded by limestone formation. It is located within the terrain area of Peninsular Malaysia Main Range Granite. Limestone is one among the five major lithologies observed in Kinta Valley, Perak (Chee Meng, 2014). Besides quarry activities, the limestone hills had also become tourist hotspot and sanctuary places for religions. The Simpang Pulai area is covered with granite, kaolin, limestone and marble, also previously a hotspot for alluvial tin mining activities.

Apart from minor granite intrusions, the calcareous rocks had form a basement beneath the alluvium throughout Kinta Valley. The calcareous rocks at Kinta Valley are dominated by limestone, following by shale, schist, phyllite and rare quartzite which interbedded with the beds of calcareous rocks (Ingham and Bradford, 1960). Part of limestone at Simpang Pulai had metamorphized to become marble.

Figure 2-2: Terrain Surrounding the Marble Hill

2.3.5 Relevant Previous Studies of Limestone as Filter Media

Previously, a study of treatment on high-manganese mine water with limestone and sodium carbonate has been published by Silva *et al.* in year 2012. 12.5 g L^{-1} of powdered limestone at 23 ± 2 °C are mixed with 0.67 g L^{-1} of sodium carbonate, Na_2CO_3 to treat the mine water using batch reaction for 60 minutes retention time in lab scale. From the results, 66.8% of iron, Fe is removed besides removing manganese and other elements. The author had proposed on the concentration of total carbonate and pH value of the mine water is key role for manganese formation and the limestone can only remove metal contaminants well when the concentration of heavy metals element in the mine water is low.

In Gangneung, Korea, the addition of limestone to AMD had been practiced since 1999, and in 10 years the pH increased from 3 to 5 with elemental concentrations of iron, manganese, magnesium, strontium, nickel, zinc and sulphur in the stream decreased. The elemental distribution of the heavy metals in the stream was mainly controlled by physicochemical processes including co-precipitation or adsorption, dilution on mixing and redox reactions as reported in Water Quality Change in AMD Streams in Gangneung Korea, 10 Years After Treatment with Limestone authored by Shim *et al.* in 2015.

Another study of high efficiency of heavy metal removal in mine water by limestone is also carried out by Yao *et al.* in year 2009 with different type of limestones in terms of limestone grade are used to treat heavy metal in mine water. The removal of cadmium, copper, nickel and zinc are reported in high efficiency. The results reported in this study as can be seen in Table 2-3 are used as reference in selection of limestone with higher grade is better for contaminants removal in the groundwater.

Table 2-3: Removal Efficiencies of Heavy Metals Using Different Geological Materials (Yao Zhigang, 2009)

Material	Grain Size (mesh)	Removal Efficiency (%)			
		Cadmium	Copper	Nickel	Zinc
Sand	20 – 30	14.4	49.5	20.2	6.1
	30 – 60	15.5	49.5	37.3	17.8
	60 - 80	31.1	89.9	72.7	16.9
Pure Limestone	20 – 30	49.1	79.8	47.7	33.3
	30 – 60	58.6	100.0	47.8	36.8
	60 - 80	66.9	100.0	50.5	40.2
Carbonaceous Limestone	20 – 30	20.2	59.6	23.5	6.1
	30 – 60	47.2	89.9	30.5	11.3
	60 – 80	66.9	79.8	40.8	25.7
Brecciated Limestone	20 – 30	28.1	49.5	37.3	17.8
	30 – 60	43.6	79.8	40.7	19.3
	60 - 80	68.0	79.8	44.2	32.7

As shown in data from Table 2-3, the smaller particle size of materials has higher efficiency in adsorption of heavy metals. Therefore, it is predicted that smaller particle size of marble used in this study will have better removal percentage of iron from the groundwater sample.

CHAPTER 3

METHODOLOGY

3.1 Outline of the Implementation Study

This project is carried out based on the outline as Figure 3-1 below. It involves all procedures and flow to be implemented during the period of study of the project to ensure the project is working smoothly.

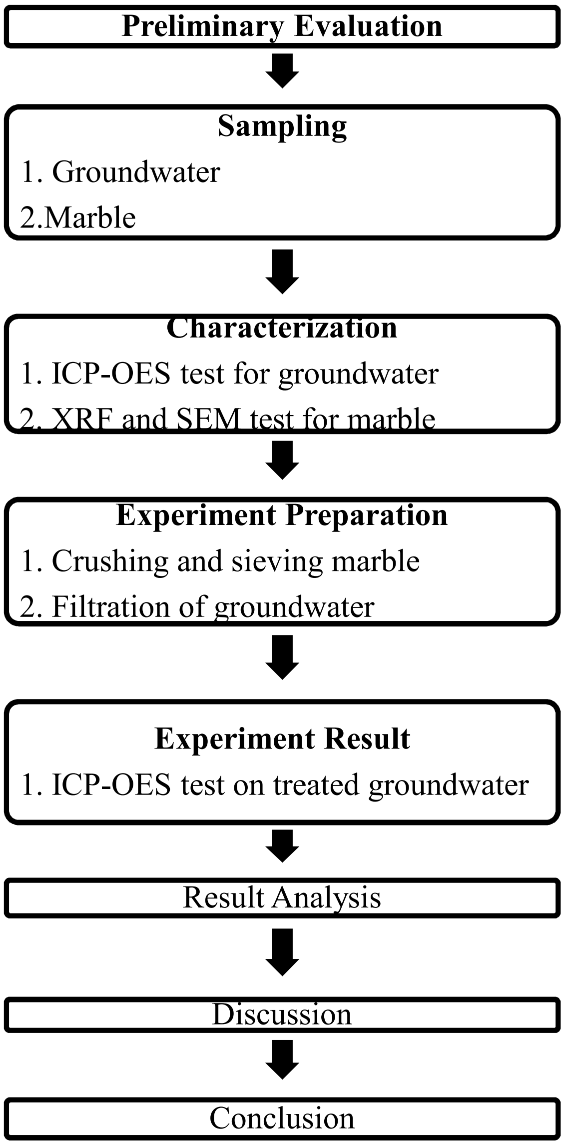

Figure 3-1: Flowchart of Project

3.2 Sample Preparation

3.2.1 Marble Sample Preparation for X-Ray Fluorescent (XRF) and Scanning-Electron Microscope (SEM) Test

The marble sample is provided by Zantat Sdn. Bhd. located at Simpang Pulai, Perak. The marble sample is crushed into fine pebbles and sand using jaw crusher and cone crusher. A John Riffle Sampler is used to sample the crushed marble, this process is important to ensure the sample is homogeneous and representable to composition of the marble.

XRF test required 30g of the marble sample in powder with size below 75 microns. The sample is ground into powder with size below 75 microns using agate mortar and sent for XRF test. The pellet of sample for XRF test is bind by resin as the adhesion of marble powder is weak and cannot be compressed into pellet in normal way.

Before conducting XRF test, Loss on Ignition (LOI) test (ASTM C25-11 19.) of the marble sample is carried out. 1 g (±0.0001 g) of the marble is weighed. The sample is then heated up to 1000 °C with temperature increment of 5 °C per minute and soaked for 30 minutes when reached 400 °C, with soaking time of 40 minutes when the temperature reached 1000 °C. LOI test is important to find out carbon content of the marble sample, so that the result of XRF can be used to calculate $CaCO_3$ content of the marble.